# ELECTROCHEMICAL DEPOSITION OF SEMICONDUCTORS FOR THERMOELECTRIC DEVICES

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## ABSTRACT

Thermoelectric microgenerators are an approach to power conversion which can deliver milliwatts to watts of power at a few to several tens of Volts. The fabrication of micrometer-scale thermoelectric elements from bulk materials is limited mechanically; however, electrochemical deposition allows fabrication of tens of thousands of elements simultaneously at scales as small as several nanometers. In order for thermoelectric microgenerators to be fabricated, approaches to the electrochemical deposition of the semiconductors used must be developed. Depositions must be stoichiometric, dense and have surface roughness less than a few micrometers. Compounds studied include $Bi_2Te_3$ and alloys such as $Bi_{2-x}Sb_xTe_3$ for near room temperature operation, and $PbTe$ and $CoSb_3$ for higher temperature operation.

## INTRODUCTION

As electronic devices for spacecraft and other applications have become miniaturized and power needs have decreased, miniature power sources have become more important. A miniature or micro-device such as a sensor, an actuator or a computer requires milliwatts to a watt of power at a few to several tens of volts. As devices shrink, power needs shrink along with them, and development of power conversion devices in which milliwatts are provided with high specific power become important. Thermoelectric power generators can be sized to fit this need.

A thermoelectric device consists of several pairs of p- and n-type elements connected electrically in series and thermally in parallel; it can be fabricated to function as a power generator, or as a cooler or heater. Shrinking the size of the thermoelectric elements (legs) makes it possible to operate at much lower currents and higher voltages, which are more compatible with electronic components, and to handle significantly higher heat fluxes [1]. A typical thermoelectric element will have a Seebeck coefficient on the order of 100-200 $\mu V/K$; thus the voltage developed across a single thermoelectric element will be on the order of 100 $\mu V$ per degree of temperature difference. By connecting several elements in series, the open circuit voltage of a device can be increased, and large temperature differentials will result in large open circuit voltages.

The route to miniaturizing thermoelectric devices is not straightforward. State-of-the-art fabrication and processing methods for semiconducting materials for thermoelectric elements have reached their mechanical limits at a leg height of 100 to 200 μm [2]. The minimum width has similar dimensions. The maximum number of legs on a single device, also limited by mechanical and manufacturing considerations, is 100 to 200, which limits the maximum open circuit voltage of a series connected device to 10 - 20 mV per degree (K) of temperature difference. This potential is sufficient for many applications; however, imposing a moderately high temperature difference such as 100 K on legs with a 1:1 aspect ratio may not be possible. A microscale thermoelectric generator with a large number of legs, a few tens of thousands, would be able to operate at much lower currents and higher voltages than a macroscale thermoelectric generator; these are the power conditions compatible with electronic components and MicroElectroMechanical System (MEMS) devices.

Figure 1 shows the relationship between leg height and specific power. Increasing the aspect ratio of the legs (leg height to leg diameter) facilitates larger ΔT.
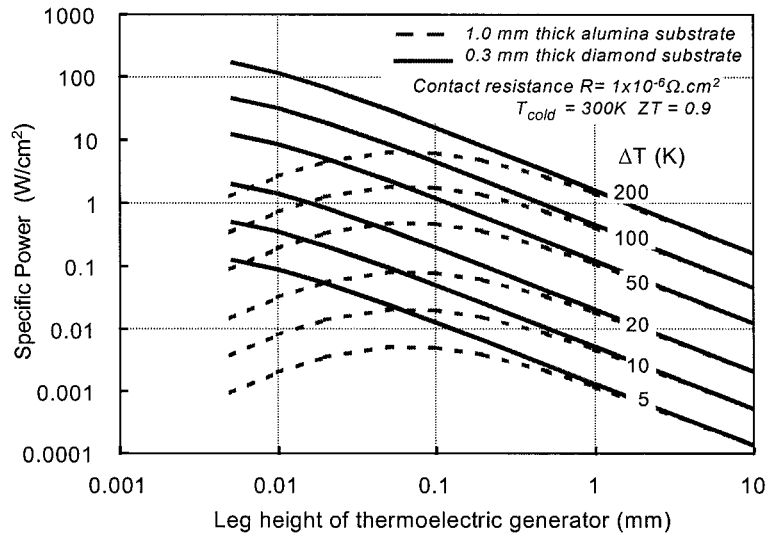


**Figure 1.** Specific power in a thermoelectric generator increases with decreasing leg height, to a maximum of about 50 μm for a device on an alumina substrate.

Fabrication methods which allow the height of a thermoelectric leg to decrease while the number of legs increases make power conversion in microdevices feasible. The approach to synthesis of thermoelectric materials discussed here is electrochemical deposition. By electrochemically depositing thermoelectric materials onto patterned substrates, devices with tens of thousands of micrometer-sized legs (20 to 60 μm high) can be made [2, 3]. Electrochemical deposition of thermoelectric elements allows fabrication of elements with dimensions as small as several nanometers [4], and it is simple, fast and inexpensive. In this work, $Bi_2Te_3$ and related alloys such as $Bi_{2-x}Sb_xTe_3$ were deposited as thermoelectric elements in arrays to make thermoelectric microdevices.

V vs. SCE. The deposition current is $\sim 0.008$ A/cm$^2$, and the growth rate $\sim 15$ μm/hour. The solution was made by dissolving high purity elements in concentrated HNO$_3$. Depositions at a more negative potential increase the growth rate, but also increase the surface roughness. Depositions at potentials more negative that -0.050 V vs. SCE were not stoichiometric, and had excess Bi. All films of Bi$_2$Te$_3$ were n-type, indicating defects of a type such as Bi vacancies.

Bi$_{2-x}$Sb$_x$Te$_3$ is an analogue of Bi$_2$Te$_3$, where Sb replaces Bi in the lattice. For p-type thermoelectric legs, the optimum composition is about Bi$_{0.5}$Sb$_{1.5}$Te$_3$, or some 12% Bi, 28% Sb, 60% Te. Compounds with a range of Bi content have been made by electrochemical deposition, using aqueous solutions containing all three elements. Sb is very poorly soluble in 1 M HNO$_3$, but Bi$_{2-x}$Sb$_x$Te$_3$ can be deposited from such a solution, although at a rate significantly slower than deposition of Bi$_2$Te$_3$. The deposition potential for the ternary compound is substantially more negative than for Bi$_2$Te$_3$; at less negative potentials, Bi and Te dominate the deposition. Deposition rates were $\sim 1$ μm/hour, and morphology was very rough and uneven. Chelating agents including EDTA, tartaric acid and citric acid were used to increase the concentration of Sb in solution; however, the change in reaction kinetics caused by the addition of chelating agents resulted in unchanged deposition rates. While these films did not deposit at a faster rate, they were significantly smoother than films made without chelating agents.

Studies of deposition potential and [Bi]/[Sb]/[Te] ratio were done to determine the conditions which will result in smooth films with 8-12% Bi. Figure 3 shows the results of this study. Bi concentration was varied (indicated by different shading on each marker) over a range of potentials. The figure shows the resulting compositions as
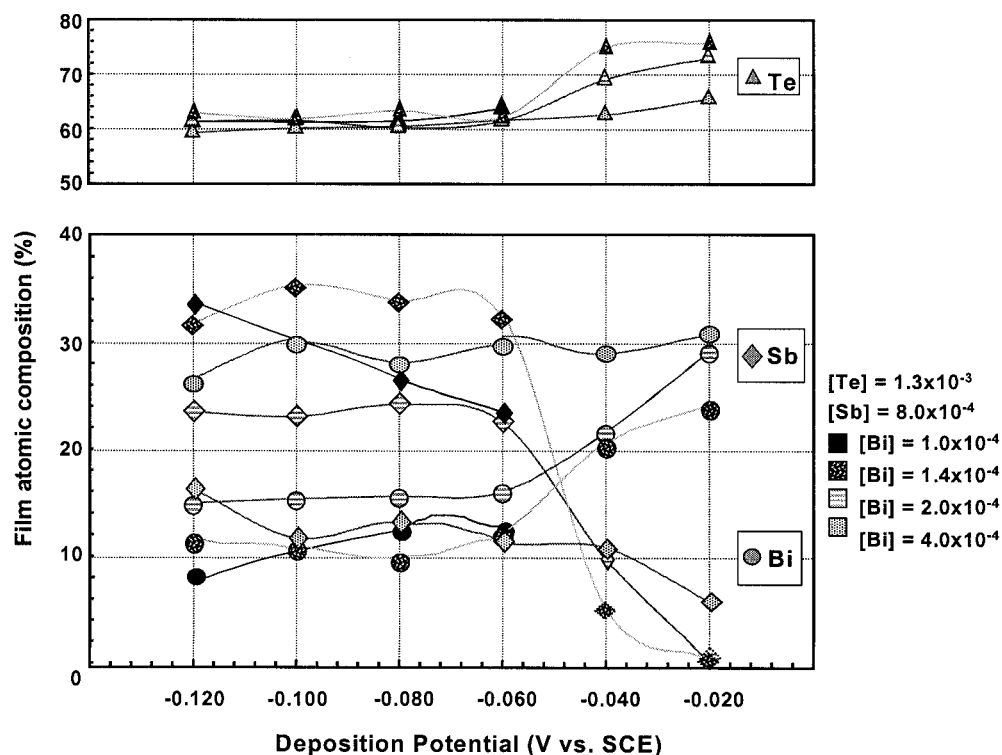


**Figure 3.** The composition of the ternary alloy Bi$_{2-x}$Sb$_x$Te$_3$ varied according to deposition potential and [Bi] in the solution while [Te] and [Sb] remained constant. Compositions are shown as atomic percent Bi (circles), Sb (diamonds), and Te (triangles), and depositions from different solutions are distinguished by shading.

atomic percent Bi (circles), Sb (diamonds), and Te (triangles). Each data series is shaded to indicate the Bi concentration in the solution.

As can be seen in the figure, depositions more negative than -0.060 V vs. SCE always resulted in Te composition ~ 60%. Depositions at a potential more negative than -0.060 V vs. SCE resulted in a mixture of Bi and Sb. There was variation in the atomic ratio of Sb/Bi, which was dependent on the solution composition. The best compositions were obtained at the highest and lowest Bi concentrations, where Sb was ~12%, ~Bi 29% and Te ~59% of the resulting film, deposited at -0.100 V vs. SCE. It was also possible to deposit using the same solutions at -0.080 V vs. SCE. Middle range solutions gave good compositions when deposited at -0.120 V vs. SCE.

The smoothest films were obtained by depositing at -0.100 to -0.120 V vs. SCE in solutions containing chelating agents. It appears that while the chelating agent allows increased concentration of Sb in the solution, it keeps slows the deposition and acts as a leveling agent by preventing Bi and Te from growing preferentially on high areas formed on the film surface. Studies are ongoing to find the best combination of chelating agents to increase deposition rate, keep film composition in the desired range and result in a smooth surface.

The ultimate goal of this work is fabrication of thermoelectric microdevices; the ability to connect several thousand pairs of thermoelectric elements in series makes it possible to produce power suitable for operating MEMS devices, i e. milliwatts of power at tens of Volts. Thermoelectric elements of dimensions 10-20 μm diameter by 50 μm high have been deposited electrochemically in wells formed by thick photoresist, and the legs connected to make a device. In such a device, both contacts and legs can be deposited electrochemically, making fabrication conditions mild and inexpensive. Figure 4 shows a view of several $Bi_2Te_3$ legs which have been grown at a density of 90,000 legs/cm$^2$.
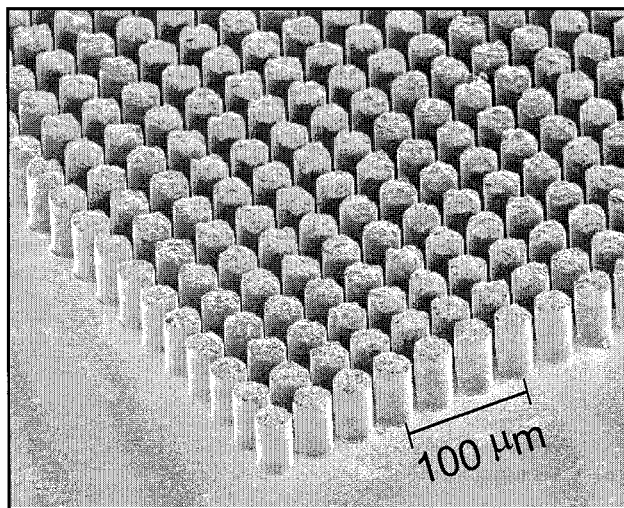


**Figure 4.** A section of electrochemically deposited $Bi_2Te_3$ thermoelectric elements 20 mm diameter x 50 mm high.

Further work in this area includes development of techniques for electrochemical deposition of thermoelectric materials in which the temperature range for optimal operation is higher than the range for $Bi_2Te_3$ type materials. $Bi_2Te_3$ and similar materials are optimal for applications at 200 - 500 K. Other materials, which operate at higher temperatures (400 - 800 K), include PbTe and $CoSb_3$. Crystalline PbTe has been deposited electrochemically, although with very rough surface morphology [4]; further studies of solution, chelating agents and temperature will be necessary to find conditions

## EXPERIMENTAL

Depositions of thermoelectric materials were done at room temperature or at slightly elevated temperature (~ 40°C) in a standard three electrode configuration, with a Pt counter electrode, Pt or Au working electrode and a Standard Calomel Electrode (SCE) reference, using a PAR Potentiostat/Galvanostat 273A. Deposition solutions contained dissolved elemental metals (Bi, Te) with a concentration on the order of $10^{-3}$ M in aqueous 1 M $HNO_3$ (pH = 0). Solutions containing Sb used chelating agents such as citrate or tartrate to keep higher concentrations of Sb in solution at pH 0. The experimental parameters varied in this study included deposition potential, temperature, and metal concentrations. Typical growth rates are 4 to 15 μm/hour.

Film thickness, surface morphology, atomic composition, crystallographic orientation and the Seebeck coefficient were measured to determine the utility of the electrochemically deposited legs. Film thickness was measured using a Dektak profilometer. The atomic composition was obtained using a Siemens D-500 x-ray diffractometer or with a Perkin Elmer 3300 DV inductively coupled plasma/optical emission spectrometer. The crystallographic orientation of the films were studied with a JEOL JXA-733 electron superprobe. The Seebeck coefficient was measured in a cross-plane direction using a simple differential thermocouple setup.

## RESULTS AND DISCUSSION

Electrochemical techniques have been developed for the growth of n-type $Bi_2Te_3$ and $Bi_2Te_{3-x}Se_x$ and p-type $Bi_{2-x}Sb_xTe_3$ compositions [3, 4]. The materials are oriented, and have Seebeck coefficients of -80 to -120 μV/K for n-type and +45 to +80 μV/K for p-type materials. These compounds are optimal for thermoelectric applications near room temperature, 200 to 500 K. This paper reports progress in developing ECD methods for obtaining these thermoelectric materials and structures, as well as optimizing their morphology and transport properties for thermoelectric microdevices.

Electrochemical deposition of semi-conductors for use as thermoelectric elements, including $Bi_2Te_3$, have been discussed by several authors [1, 2, 5-7]. Studies of optimization of composition and morphology resulted in smooth, oriented films, as shown in Figure 2. Studies included variation of [Bi]/[Te] ratio and deposition potential. It was found that the smoothest stoichiometric films were made with solution where [Bi]=$8x10^{-4}$ M and [Te]=$1x10^{-3}$ M in 1 M $HNO_3$ at a potential of -0.01
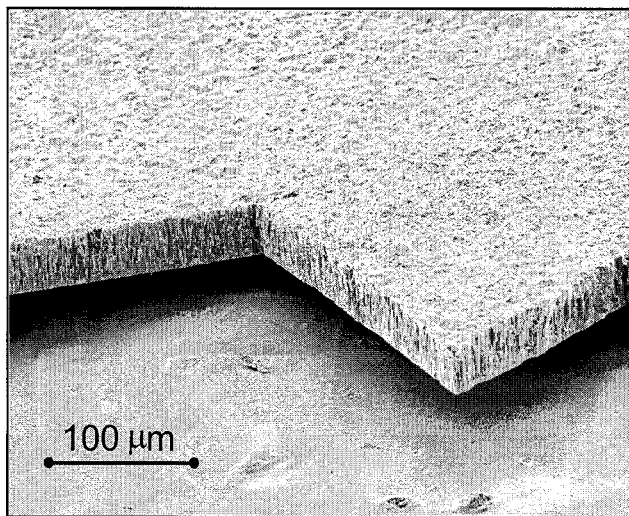


**Figure 2.** A film of $Bi_2Te_3$ deposited from 1 M HNO solution of $8x10^{-4}$ M Bi and $1x10^{-3}$ M Te, at -0.010 V vs. SCE.

for depositing PbTe that is smooth enough to be used in a microdevice. Smooth films of Co and Sb have been co-deposited in stoichiometric concentrations for $CoSb_3$, with short range order, but with poor reproducibility. Studies of deposition of both Sb and Co as well as codeposition are ongoing in order to understand the conditions for deposition and the conditions which might interfere with reproducibility.

## ACKNOWLEDGMENTS

## REFERENCES

1. M. Muraki and D. M. Rowe, *Proc. Xth Int. Conf. on Thermoelectrics*, Cardiff, Wales, UK, 174 (1991).

2. J.-P. Fleurial, *et al.*, Thermoelectric Materials 1998, T. M. Tritt, M. G. Kanatzidis, H.B. Lyon, and G. D. Mahan, eds., MRS Volume 545 (1998).

3. J.-P. Fleurial, *et al* , Thermoelectric Materials 2000, T. M. Tritt, M. G. Kanatzidis, G. Nolas, and G. D. Mahan, MRS 2000 Spring Meeting Symp. Proc., (2000).

4. J.-P. Fleurial, *et al, Proceedings of the 34th Intersociety Energy Conversion Engineering Conference*, 99-2569 (1999).

5. R. K. Pandey, S. N. Sahu and S. Chandra, Handbook of Semiconductor Deposition, M. Dekker, New York (1996).

6. M. Takahashi, Y. Katou, K. Nagata and S. Furuta, *Thin Solid Films*, **240**, 70 (1994).

7. P. Magri, C. Boulanger and J. M. Lecuire, *Proc. XIII Intl. Conf. on Thermoelectrics*, B. Mathipraksam, ed., Part I, 1994.